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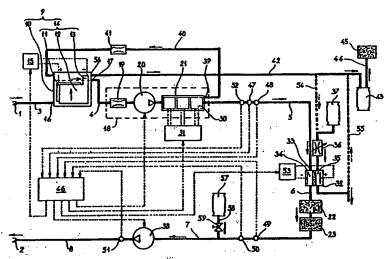
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(54) Title: EQUIPMENT FOR REGENERATION OF LIQUIDS CONTAMINATED BY ORGANIC SUBSTANCES, MEASURING DEVICE AND METHOD FOR MEASURING OF ORGANIC MATERIAL AND HYPOCHLORITE ION CONTENT



(57) Abstract

An equipment serving for regeneration of fluids, being provided with an electrolyzer (9) and an active charcoal filter (22), wherein the electrode system (14) of the electrolyzer (9) consists of plates arranged parallel with each other, of which every other sheet connected with each other constitutes the anodes (11) and cathodes (12) respectively, each cathode (12) being extended upwards on its discharge-pipe side by a narrow strip (13), the discharge pipe (17) connection being at the same level as, and perpendicular to, said strips (13), wherein the connection of the admission pipe (16) of the liquid onto the electrode system is adapted in the vicinity of the discharge pipe (17) connection farthest away from the electrolyzer, and viewed from the direction of the inlet pipe connection (1) toward the outlet pipe connection (2), the electrolyzer (9) comes first, and the active charcoal filter comes later, and a degassing assembly (18) is inserted between them, further a zeolite filter (23) is installed after the active charcoal filter (22). A measuring device for measuring the organic material and hypochlorite ion contents, consisting of a vessel (60) with a liquid inlet (68) and a liquid outlet (69), a pin electrode (65), a polarizing electrode (66) and a reference electrode (67), wherein the polarizing electrode (66) is connected to a continuously variable potential supply unit (70), said liquid inlet (68) being arranged in the vicinity of the point (71) of the pin electrode (65).

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INTERNATIONAL SEARCH REPORT

International application No. PCT/HU 94/00026 CLASSIFICATION OF SUBJECT MATTER IPC⁶: C 02 F 9/00, 1/461, 1/28 According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC⁶: C 02 F 9/00, 1/461, 1/28 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI(L) C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Category* Relevant to claim No. Α US, A, 5 174 879 (GADKE-FUHRMANN) 29 December 1992 (29.12.92), claims 1,12; fig. 1 Patent Abstracts of Japan, unexamined applications, A section C, vol. 7, no. 161, 15 July 1983 (15.07.83), The Patent Office Japanese Government, page 81 C 176, no. 58-70 881 (NIHON GIJUTSU). P,A Patent Abstracts of Japan, unexamined applications, section C, vol. 18, no. 248, 12 May 1994 (12.05.94), 1 The Patent Office Japanese Government, page 140 C 1198, no. 6-31 278. Further documents are listed in the continuation of Box C. Х See patent family annex. Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance later document published after the international filing date or priority date and not in conflict with the application but cited to understand "E" .carlier document but published on or after the international filing date the principle or theory underlying the invention document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive considered novel or cannot be considered to involve an inventive step when the document is taken alone document referring to an oral disclosure, use, exhibition or other document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination document published prior to the international filing date but later than the priority date claimed being obvious to a person skilled in the art "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 07 Decemb r 1994 (07.12.94) 28 December 1994 (28.12.94) Name and mailing address of the ISA/AT AUSTRIAN PATENT OFFICE Kohlmarkt 8-10 Authorized officer Vienna 1/53424/535 A-1014 Facsimile No. Wilfling r e.h.

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(57) Abstract

(30) Priority Data:

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The invention relates to an equipment serving for regeneration of fluids, primarily of dialysis liquids, contaminated with organic materials, the equipment being provided with an electrolyser (9) and an active charcoal filter (22), wherein the electrode system (14) of the electrolyser (9) consists of plates arranged parallel with each other, of which every other sheet connected with each other constitutes the anodes (11) and cathodes (12) respectively, each cathode (12) being extended upwards on its discharge-pipe side by a narrow stripe (13), the discharge pipe (17) connection being at the same level as, and perpendicular to, said stripes (13), wherein the connection of the admission-pipe (16) of the liquid onto the electrode system is adapted

in the vicinity of the discharge-pipe (17) connection farthest away from the electrolyser, and viewed from the directon of the inlet pipe connection (1) toward the outlet-pipe connection (2), the electrolyser (9) comes first, and the active charcoal filter comes later, and a degassing assembly (18) is inserted between them, further a zeolite filter (23) is installed after the active charcoal filter (22). The invention relates, further, to a measuring device for measuring the organic material and hypochlorite-ion contents, consisting of a vessel (60) with a liquid inlet (68) and a liquid outlet (69), a pin electrode (65), a polarizing electrode (66) and a reference electrode (67), wherein the polarizing electrode (66) is connected to a continuously variable potential supply unit (70), said liqui inlet (68) being arranged in the vicinity of the point (71) of the pin electrode (65). Finally, the invention also relates to a method for combined measurement of organic material and hypochlorite-ion contents.

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EQUIPMENT FOR REGENERATION OF LIQUIDS CONTAMINATED BY ORGANIC SUBSTANCES, MEASURING DEVICE AND METHOD FOR MEASURING OF ORGANIC MATERIAL AND HYPOCHLORITE ION CONTENT

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TECHNICAL FIELD

The invention relates to an equipment by means of which fluids, such as a dialysis liquid, polluted by organic substances can be regenerated which is provided with an electrolyzing device and an active charcoal filter. Further, the invention relates to a method and a signal transmitter suitable for combined measurement of organic substances and the hypochlorite-ion concentrations by introducing the fluid containing the organic substance and hypochlorite ion into an electrochemical reservoir containing a pin electrode, a polarizing electrode and a reference electrode and polarizing the pin electrode with the polarizing electrode.

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BACKGROUND ART

In many fields of related technology trouble is often caused by the water contaminated by organic substances. This manifests itself in some cases as a problem of environmental pollution or, in other cases, as excessive water consumption. One of such specific fields is the artificial kidney treatment.

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It is known that the dialysis liquid consumption of artificial kidney machines used at present amount to about 150 to 200 liters per treatment, the waste liquid being discharged into the sewage system. (An exception is the equipment of the REDY system, which however, just for the same reason, is incapable of furnishing all

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functions provided by other types of artificial kidney apparatus. Regeneration of the dialysis liquid is important not only from economic aspects, but also from that of environmental protection, and neither the important preliminary condition of regenerating the dialysis liquid used in preliminary artificial kidney treatment can be neglected in arid regions.

The dialysis liquid is a physiological solution containing the metabolic products of the kidney (urea, creatinine, uric acid, phosphates, potassium etc.). The main mass of toxins is represented by urea. Removal of these substances can be achieved by means of several methods, such as the use of sorbents of various kinds, electrochemical oxidation, chemical decomposing, and combinations thereof.

The method of using sorbents was widely used in the 60ies and 70ies, but the poor absorption of urea, even by active charcoal, has soon become evident. Therefore, in the REDY method, the use of sorbents was combined with previous decomposition of urea into CO₂ and NH₃ by enzymes, and then, by adsorbing NH₃ by zirconium phosphate. The phosphate content of the dialysis liquid is bound by zirconium oxide and other toxins by active charcoal.

To improve the efficiency of adsorption various methods have been developed. E.g. in Patent Specification JP-61-3060 combination of oxidized starch and an organic compound of large molecule size has been proposed as adsorbent, whereas, according Patent Specification SU-52273 the adsorbent is to be selected from the magnesium silicate, magnesium trisilicate, aluminium oxide group and, according to the proposal described in a Soviet author's certificate SU-1012918, the active charcoal is treated

with a metal of the platinum group using quantities of 0.01 to 0.1 % by weight. In Patent Specification US-3.827.961 an electrically conductive adsorbent, e.g., active charcoal, is employed which is energized by a voltage led through a zigzag electrode to enhance adsorption.

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From the many attempts to find a solution it can be felt that no satisfactory cleaning can be achieved by adsorption alone. This is due to the difficult adsorption of urea, mainly when also compounds consisting of smaller-size molecules are present. That is why chemical and electrochemical methods have stepped into the foreground.

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In Patent Specification US-3.827.975 a method has been presented where hypochlorite is added to the dialysis liquid after passing it through an active charcoal layer. The hypochlorite as strong oxidizing agent oxidizes the urea to nitrogen and carbon dioxide in a reactor. Since the hypochlorite has a toxic effect on a human organism, its dosing is controlled by a hypochlorite sensor mounted at the reactor outlet.

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A similar chemical process takes place in the arrangement proposed in US Patent Specifications 3.909.977 and 3.935.092 but in both cases the dialysis liquid is subjected to electrolysis after the active charcoal treatment, by which hypochlorite is reproduced by using the NaCl content of the liquid. Further on, the process is identical with that outlined above. Here, by analogy, the electrolytic process is controlled by the hypochlorite sensor.

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Since with both methods, risk of hypochlorite remaining in the regenerated fluid exists, ascorbic acid is added to neutralize such residues.

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Within experiments with the electrolytic process it has been found that by applying low anode potential the urea can be oxidized to form a non toxic product, but this process takes place at a very slow rate. In US Patent Specifications 4.663.006 and 4.846.950 cyclic polarization has been proposed, but this method is still too slow. Finally, the adoption of high anode potentials proposed in author's certificate SU-4366630 has provided the solution, by means of which direct oxidation of urea can be obtained already during the electrolytic process. On a platinum surface this takes place according to the following equation:

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$$(NH_2)_2 CO + H_2O \rightarrow N_2 + CO_2 + 6H^4 + 6e^-$$

This process, however, is associated with heavy hypochlorite-ion segregation as consequence of chlorine-ion deposition on the anode, as shown here below:

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$$2Cl^{-} \rightarrow Cl_{2} + 2e^{-}$$

$$Cl_{2} + H_{2}O = OHCl + H^{+} + Cl^{-}$$

$$2H_{2}O + 2e^{-} \rightarrow H_{2} 2O^{-}$$

$$HOCl + 2OH^{-} \rightarrow ClO^{-} + H_{2}O$$

The other anode process associated with the above is the segregation of oxygen.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

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From the description it will be apparent to that pollution caused by organic substances cannot be fully eliminated by the adsorption process, while the electrochemical method raises a new problem resulting from the hypochlorite-ion formation.

While the hypochlorite-ion formation represents the hardest problem, the electrochemical process exhibits a further drawback. Direct oxidation of the various organic substances takes place only at a specific anode potential characteristic of the material concerned. As the adjustment of anode potential is characteristic of the contaminating substance present in the largest percentage (this being the urea in dialysis liquids), the other organic substances do not reach the stage of perfect oxidation, but intermediate compounds are formed. The molecules of these organic fragments are of smaller size than that of the original substance. This causes concern because, as shown by experience, the smaller a molecule, the higher its toxicity.

To sum up: adsorption is not perfect, and within electrolysis hypochlorite ions and toxic organic fragments are formed. Thus, the object of the invention is to propose a method eliminating this problem and being capable of performing perfectly the regeneration of the liquid. The following recognition has led to the proper solution.

Although absorption preceding electrolysis removes part of the organic substances, it is quite sure that several kinds of such pollutants get into the electrolyzing apparatus, so the formation of organic fragments is unavoidable. Therefore, adsorption before electrolysis can safely be omitted, whereas the adsorption after the electrolysis is by all means indispensable.

Within electrolysis not only formation of hypochlorite ions, but also their recombination can take place, according to the following reaction:

$$ClO^{-} + 2H^{+} + 2e^{-} \rightarrow Cl^{-} + H_2O$$

By letting the liquid to pass between the extensions of the cathodes, at the end of the electrolysis the hypochlorite ions can be regenerated. Unregenerated hypochlorite-ions step into reaction with the carbon of the active charcoal filter, and CO₂ is released. Thus, the adsorption after electrolysis is of advantage also regarding binding the hypochlorite ions.

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Within electrolysis, however, also a gas formation takes place in the liquid, which - as it is known - would impair the adsorption capability of the active charcoal filter. Their use in immediate succession would reduce the efficiency of regeneration. Therefore, the fluid has to be degasified.

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Finally, the use of zeolite filling in the ion exchanger not only enhances regeneration, but it exchanges the potassium ions by sodium ions that may have got into the dialysis liquid.

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To keep under control the regenerating process of fluids contaminated with organic matter, i.e., to prevent insufficient removal of organic pollution or excessive formation of hypochlorite ions, a continuous checking of their concentration is indispensable.

For measuring the concentration of organic substances or, to be more precise, that of urea, according to the methods proposed by others, the measuring electrode, reference

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electrode and polarizing electrode are each accommodated in separate vessels. The vessels are filled with electrolyte solution. The fluid to be measured is let to flow under the vessels. The bottom of the vessel containing the measuring electrode is separated from the fluid to be measured by a diaphragm bonded with a layer of ureaze and a layer of ammonium ion sensitive diaphragm, whereas the bottoms of the other two vessels by a dialysis diaphragm. According to Patent Specification US-4.476.005 describing the above measuring assembly, the method is based on quantitative determination of ammonium ions.

Similarly, the method presented in Patent Specification US-3776.819 is also based on quantitative determination of ammonium ions, but here only two electrodes are employed.

Since with both methods the quantity of ammonium ions raised by urea on the diaphragm bonded with an enzyme, both procedures are very slow, so they are unsuitable for the process control of regenerating liquids polluted by organic substances.

An equipment also comprising two electrodes and a diaphragm is described in Patent Specification US-4.614.577. Here, a proposal is made to improve the measuring accuracy by means of accurately specifying the characteristics of the diaphragm. Concentration of organic substances is brought into relation with the amount of current.

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Another similar process for measuring sodium hypochlorite is disclosed in Patent specification US-4.605.47. The measuring assembly comprises three electrodes, where the measuring electrode is a golden wire. The polarizing electrode and the reference electrode are kept at constant potential, and the current flow is measured. This is proportional to the sodium hypochlorite concentration. Thus, the measuring method tries to determine the hypochlorite-ion content in an indirect way, with an unsatisfactory result.

As it can be seen, the methods consisting of measuring either the quantity of organic substances or that of the hypoclorite-ion content are based on using an electrochemical assembly comprising several electrodes, but, due to their inaccuracy or slowness, they are unsuitable for accurate and quick process control.

DISCLOSURE OF INVENTION

Our objective has been to develop such signal transmitters which are free from the drawbacks outlined above. The solution is based on the recognition that, on the one hand, the measurement of the content of organic substances can be substituted by measuring the oxygen adsorption taking place at anode potential, because the organic substance content puts a restraint on the oxygen absorption. On the other hand, conclusion on the hydrochlorite content at anode potential can be drawn from the current produced by the restoration of hydrochlorite-ion concentration, this current being the result of the following reaction:

$$ClO^{\circ} + H_2O + 2e^{-} \rightarrow Cl^{\circ} + 20H^{\circ}$$

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$$ClO^{-} + 2H^{+} + e^{-} \rightarrow HClO + 1/2 H_{2}$$

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The organic-substance content and the hypochlorite-ion content can thus be measured also by a single electrochemical means, because the electrochemical processes take place in separate half periods. It has also been recognized that the organic-substance content is in close relation with the time delay of oxygen adsorption, whereas the hypochlorite-ion content is linked with the quantity of current pertaining to the regeneration. Finally, as we found that a continuous flow of liquid in the immediate surrounding of the measuring electrode has been found improving the accuracy of measurement considerably.

The invention is, thus, an equipment suitable for regenerating liquids, such as a dialysis liquid, polluted with organic substances, provided with an electrolyzing device and an active charcoal filter, and characterized by an electrode system of the electrolyzer composed of plates arranged parallel with each other and every other of them being connected with each other to form the anodes and cathodes, the cathodes being extended upwards by narrow stripes on the outlet side, the outlet of the liquid is arranged at the level of said stripes perpendicular to them, while the liquid is discharged onto the electrode system at a point laying farthest away from the outlet, and when viewing in the direction of flow from the inlet connection toward the outlet connection, the electrolyzer comes first and the active charcoal filter comes later, with a degassing assembly inserted between them, furthermore a zeolite filter is accommodated after the active charcoal filter.

In an advantageous embodiment of the equipment complying with the invention, the degassing assembly consists of a throttle connected in series in the direction of fluid

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flow, a pump and a reservoir of a cross-sectional area relatively large as compared to that of the piping.

In another advantageous embodiment of the equipment complying with the invention, a second pump is inserted between the zeolite filter and outlet-pipe connecting fitting.

In a third advantageous embodiment of the equipment complying with the invention a cooler is inserted at any point between the electrolyzer and outlet-pipe connection or second pump if installed.

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With the fourth advantageous embodiment of the equipment complying with the invention, the cooler is integrally built with the reservoir of the degassing assembly.

The fifth advantageous embodiment of the equipment complying with the invention is characterized by the reservoir of the degassing assembly being of enclosed design and provided above the normal liquid level with a gas outlet connected through a pipe into the electrolyzer at a point above normal liquid level on the liquid-inlet side, and by having a throttling fitting inserted in the connecting pipe:

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The sixth advantageous embodiment of the equipment complying with the invention comprises an overflow port inserted between the electrolyzer and degassing assembly, or between the degassing assembly and outlet-pipe connection, or second pump if installed, where the delivery output of said second pump is lower than that of the pump of the degassing assembly.

In the seventh advantageous embodiment of the equipment complying with the invention the overflow port is arranged on the outlet side of the electrolyzer above normal liquid level, said port being connected into an enclosed liquid reservoir with its highest point communicating with the ambient atmosphere through an active charcoal filter.

In the eighth advantageous embodiment of the equipment complying with the invention, an electrochemical corrector is inserted between the degassing assembly and active charcoal filter.

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In the ninth advantageous embodiment of the equipment complying with the invention the active charcoal filter or zeolite filter is designed so that the filter housing is a plastic bag in which the filter filling is placed between two plastic nets with the connecting pipes inserted between the sealed ends of the plastic bag and plastic nets.

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Characteristic of the tenth advantageous embodiment of the equipment complying with the invention is an organic substance sensor inserted anywhere between the inlet-pipe connection and the action charcoal filter, and a hypochlorite sensor is inserted anywhere between the electrolyzer and the active charcoal, further, at least one temperature detector, one pH-sensor and one pressure sensor, the latter three being connected to the inputs of an electronic control unit, whereas the respective outputs of the control unit issue regulating pulses to the supply unit of the electrolyzer, to the pump of the degassing assembly, to the cooler and to the second pump, if there is one, and to the supply unit of the electrolytic corrector.

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The invention relates, further, to an electrochemical measuring device for the measurement of organic material and hypochlorite-ion concentration, consisting of a vessel, a pin electrode, a polarizing electrode and a reference electrode, said vessel being provided with a liquid-inlet and a liquid-outlet connection and characterized by the polarizing electrode being connected to a continuously variable potential supply unit, and the connections of the liquid admission pipe and/or liquid discharge pipe are located in the vicinity of the point of the pin electrode.

In an advantageous embodiment of the electrochemical measuring device the liquid compartments around the reference electrode and pin electrode are separated from each other, said compartments being connected through a solid-electrode bridge, with the point of the pin electrode accommodated in the vicinity of said solid-electrode bridge.

Finally, the invention also relates to a method for combined measurement of the organic material and hypochlorite-ion content, where within said measurement the liquid containing said organic material and hypochlorite-ion is led into an electrochemical vessel containing the pin electrode, polarizing electrode and reference electrode, the method being characterized by cyclically polarizing the pin electrode by the polarizing electrode within the anode-cathode range, and steadily increasing, first, the potential on the pin electrode up to the adsorption potential of oxygen and measuring the time required to reach a predetermined value of current, said time being proportional to the organic material content, then by steadily reversing the polarity of the pin electrod from anode potential to cathode potential, and recording the value of current measured in the potential range of hypochloride-ion restoration, and

maintaining a steady flow of the liquid under test around the point of the pin electrode during the measurement.

BRIEF DESCRIPTION OF DRAWINGS

- The invention will now be described, by way of example illustrated in the attached drawings, where:
 - Figure 1 is the circuit diagram of the equipment complying with the invention.
 - Figure 2 and 3 show two sections of the discardible filter
 - Figure 4 is a sketch of the combined signal transmitter, a measuring device
- 10 Figure 5 illustrates the E-I diagram of the polarization of the combined signal transmitter.

BEST MODE FOR CARRYING OUT THE INVENTION

In Figure 1 the circuit diagram of equipment is shown that has been built for regenerating the dialysis liquid of an artificial kidney apparatus. It is thought, namely, that an invention can be best presented by describing realized operating equipment built according to the invention. For the sake of authentic description, therefore, several elements and units appear, which are - neither in principle, nor in practice - necessary for carrying out the invention, but which are indispensable when to be used with an artificial kidney machine. All this does not cause any confusion in understanding the invention, notwithstanding it will be tried to keep in view the order of importance of the various units. It should be pointed out that the equipment to be described here is neither an exclusive form of the invention, nor an exclusive field of its application.

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The equipment illustrated in Figure 1 can be coupled to the dialysis liquid system of an artificial kidney machine (not shown in the figure) through inlet-pipe connection 1 and outlet-pipe connection 2. As it is known, the basic task is to remove the organic matters and toxic substances from the dialysis liquid during its regeneration, which is done by means of electrolysis and filtering.

The inlet-pipe connection is led through a pipeline 3 to the electrolyser cell 10 of an electrolyser 9. Anodes 11 and cathodes 12 consisting of metallic sheets arranged parallel with each other are immersed in said electrolyzer cell 10. Material of the sheets is platinum applied to a titanium base. Every other sheet connected form together the anodes 11 and cathodes 12. The surface of cathodes 12 is increased by vertical stripes 13 as if extending one of their vertical edges. The electrode system 14 consisting of anodes 11 and cathodes 12 is connected to a supply unit 15.

The electrode system 14 is arranged in the electrolyser cell 10 so that the discharge pipe 17 of the liquid is connected to the side of the electrolyser cell at the level of stripes 13 whereas the admission pipe 16 is attached to the cell farthest away from the discharge-pipe connection 17 at the lowest part or in the bottom of the electrolyser cell 10 on the side opposite to said discharge-pipe connection 17. The electrode system 14 is arranged parallel to the direction of flow defined by the connections of admission-pipe 16 and discharge pipe 17, whereas the stripes 13 stand upright assuming a position perpendicular to the direction of flow defined by the discharge pipe connection 17.

The discharge pipe 17 of the electrolyser 9 is connected through pipelin 4 to a degassing assembly 18. The design of the degassing assembly 18 may take different forms, e.g., a vessel filled with Raschig rings or with granules, an ultrasonic degassing device etc. In the equipment designed by us the degassing assembly 18 consists of a throttle 19, a pump 20 and a reservoir 21 connected is series in the sequence defined by the direction of flow of the liquid. The cross-sectional area of reservoir 21 is considerably larger than that of the pipeline 4.

Through pipelines 5 and 6, an active charcoal filter 22 and a zeolite filter 23 connected in series are coupled the degassing assembly. Said filters may be of any known design. The task being of biomedical nature, where sterility is very important, either some solution lending itself to easy sterilization or the use of discardible means is required. In Figures 2 and 3 an arrangement of the latter kind is shown.

The filter housing consists of a plastic bag divided essentially into three compartments. The filtering medium 26 is filled into the space confined by the two plastic nets 25 through a filling orifice that is then sealed by welding. Into each of the lower and upper edges of the plastic bag 24, fully separated from the inner space of the latter, a PVC pipe 29 is attached by welding for the sole purpose of fixing the bag into the equipment. Otherwise, the material of the plastic bag 24 and of the pipes 28 is identical with that of the infusion fittings used in medical practice.

The zeolite filter 23 is connected to the discharge pipe connection 2 through pipelines 7 and 8.

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In principle, the units described here would render the equipment suitable for maintaining the artificial kidney machine in operation under a permanent load. Since the artificial kidney machine is not designed for using regenerated liquid, but for being operated with purified water treated in an ion exchanger, besides purity, properties of the regenerated water have to be restored as well. In principle, this could be done after the cleaning process, but inclusion of said other restoration measures into the cleaning process advantageously support achievement of the principle offered by the invention.

From the point of view of restoration an important physical property of the regenerated liquid is of temperature. Adjustment of this parameter is required because the liquid is heated in the electrolyser 9. Therefore, inclusion of a cooler 30 is required. Regarding its design, this apparatus may be of any kind and could be arranged anywhere in the system. Yet, in the actual equipment, it has been located at the reservoir 21 of the degassing assembly 18. The advantage of this arrangement results from the fact that a liquid can keep a smaller amount of gas in dissolved state at lower temperature, so the efficiency of degassing is improved by cooling. Otherwise, the cooler 30 consists of semiconductor-type Peltier cells attached to the side of reservoir 21 that are connected to supply unit 21.

The other property requiring restoration is the pH-value of the liquid. This is achieved by the electrochemical corrector 32 inserted between pipelines 5 and 6. The electrochemical corrector is of a well-known design. Anode space 33 and cathode space 34 are separated by a diaphragm 35, in our case made up of a ceramic material of ZrO₂ content. The cath de space 34 is connected with pipelines 5 and 6, whereas

the anode space 35 through a control valve 36 with a liquid container 37. The liquid leaving the anode space 35 is discharged into the sewage system.

Since the dialysis liquid may only be fed into the artificial kidney machine at a specified pressure, a second pump is installed before the outlet-pipe connection between the pipeline 7 and 8.

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In the artificial kidney treatments the required flow of liquid depends on the type of treatment, therefore, since the regenerating equipment and artificial kidney machine constitute a closed circulation system, a possibility of disposing the excess amount of liquid has to be provided for. For this purpose, either a buffer tank or an overflow outlet has to be inserted into the system. In principle, these could be fit anywhere, still, for the sake of controllability of the system, it is appropriate to adapt such a facility between electrolyser 9 and second pump 38. (Obviously it cannot be arranged between the internal fittings of the degassing assembly 18 employed by us.)

The removal of gases developing during the electrolysis has also to be catered for, since first that is why the degassing itself is necessary.

The two tasks have been solved by a method accomplishing both in the following combined way:

The reservoir 21 of the degassing fitting 21 is provided with a gas discharge orifice 39 located above the normal liquid level. This is purposefully at that end of reservoir 21 where also the pipeline 6 is connected. The gas discharge orifice 39 is connected,

through a pipeline 40 into which a throttle 41 is inserted, with electrolyser 9 at a point above normal liquid level on the side where the admission pipe 16 of the liquid is connected. On the cell 10 of electrolyser 9, on the side of the discharge pipe connection 17, above normal liquid level an overflow orifice is provided to which a pipeline 42 is attached. The other end of said pipeline 42 is led into a liquid container 43. The liquid container is expediently a liquid collecting bag commonly used in medical practice. The highest point of the liquid container 43 is connected with the ambient atmosphere by means of a pipeline 44 and through an active charcoal filter 46.

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Finally, when required by treatment technology, supply of physiological salt solution may also become necessary. A liquid reservoir 57 containing said solution is connected through pipeline 58 into pipeline 7. A manually operated shut-off fitting 59 is inserted in pipeline 58.

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Obviously, in the system described here so many parameters have to be considered and regulated that the task cannot be accomplished by visual observation and manual intervention. Regulation is rendered especially difficult by the steadily changing load imposed on the equipment, gradually decreasing during an artificial kidney treatment. Therefore, the equipment has been provided with an automatic control unit 46.

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The parameters to be controlled or to be kept at specified levels are the organic material content, the hypochlorite-ion content, the pH-value, the temperature and the pressure. Correspondingly, to the inputs of control unit 46 an organic material signal

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transmitter 47, a hypochlorite signal transmitter 48, a temperature signal transmitter 49, a pH signal transmitter 50 and a pressure signal transmitter 51 are connected.

The organic material signal transmitter 47 may be inserted anywhere between inletpipe connection 1 and outlet-pipe connection 2, the hypochlorite signal transmitter 48, the temperature signal transmitter 49 and the pH signal transmitter anywhere after the electrolyzer 9, whereas the pressure signal transmitter may only be adapted after the second pump 38. Since, however, the pH value is influenced by the temperature, the temperature signal transmitter 49 has to be inserted before the pH signal transmitter 50, moreover, for similar reason, also the organic material signal transmitter 47 and the hypochlorite signal transmitter 48 should expediently be accommodated beside each other and installing a further temperature signal transmitter 52 also connected to an input of the control unit 46.

The outputs of the control unit 46 are linked up with the supply unit 15 of electrolyser 9, with the driving motor of pump 20, with the supply unit 31 of cooler 30, with the supply unit 53 of the electrochemical corrector 32 and with the driving motor of the second pump 38.

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Considering that the signal transmitters themselves are known elements, just as the controlled fittings, both the selection of them and the design of electronic circuitry of the control unit 46 are a routine task for a person skilled in the art, they are no new part of the invention, so their detailed description can be omitted. (It should be noted that the motors f pump 20 and second pump 38 are pulse controlled. This is why no

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connection through a safety valve between input and output ends of the liquid system is provided.)

The design of the equipment has been matched to the requirements of a DIAMATE HDC type artificial kidney machine. With this apparatus the required flow velocity of the liquid is 400 to 600 ml/min, expediently 500 ml/min. Total quantity of liquid circulating in the closed system consisting of the dialysis liquid system of the artificial kidney machine and of the equipment covered by the invention is 1.5 liters. 90 % of the organic material content of the dialysis liquid leaving the artificial kidney machine is urea, the quantity of which is 3 g/l at the beginning of the treatment, reducing to about 0.1 g/l at its end. Further significant ingredients present in the liquid are creatinine, uric acid, phosphates and some other toxins and potassium ions.

During the regeneration process, according to European standards, and assuming the most general 4-hour duration of an artificial kidney treatment, the quantity of contaminations to be decomposed in 1 hour is on the average 10 g urea, to 2.5 g creatinine, 1.5 g uric acid and 1.2 g phosphate, and 1.2 g of K⁺ ions are to be extracted.

The fact already mentioned has to be considered: the organic material content reduces during artificial kidney treatment. With conventional dialysis, this reduction is not linear, since the organic substances present in the blood can be extracted quickly, but after that any further amounts are released by the human organism with difficulty only.

This imposes a strain on the patient. This problem can also be solved by the regeneration, namely if regeneration is less than 100 %, i.e. part of the organic

material content is recirculated into the artificial kidney machine, the abstraction is rendered steadier. So, although the regeneration could be performed immediately and completely, full regeneration can be achieved only once, at the very end of the process of artificial kidney treatment.

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The liquid entering the equipment gets first into the electrolyser 9. Ten ampers current is fed by a supply unit 15 to ten anodes 11 and to ten cathodes 12, each of 0.5 m² overall surface and spaced 0.4 mm apart, producing a high, 2.2 to 2.9 volt anode potential measured on the silver-silverchloride reference electrode.

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During the electrolysis approx. 60 % of the organic material becomes fully decomposed, a small part of the remainder leaves the electrolyser 9 as organic fragment (as intermediate compound of chemical transformation produced by electrolysis), whereas the major part of the remainder is discharged in unchanged state.

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During electrolysis hypochlorite cons are formed in an amount inversely proportional to the quantity of decomposed organic substances. While flow, the liquid containing hypochlorite ions get within the electrolyser 9 between the stripes 13 of cathodes 12. Here, major part of the hypochlorite ions is transformed, and such a liquid will leave the electrolyser 9 that will have a maximum hypochlorite ion content of 100 mg/l. During electrolysis the temperature of the liquid rises by 2°C.

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Hereupon, the liquid gets into the degassing assembly 18. Here, the liquid is delivered by pump 20 of 700 to 800 ml/min through an -500-Hgmm throttle into reservoir 21.

Under the flect of the pressure reduction the gases produced during electrolysis

escape from the liquid, and in reservoir 21, where flow of the liquid dec lerates due to the increase of cross-sectional area by 15-times with respect to that of pipeline 4, and bubbles emerge from the liquid. Simultaneously, the liquid is recooled to inlet temperature by cooler 30.

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The degassed, recooled liquid leaves the reservoir 21 through pipe 5, while the gas gets through gas discharge orifice 39 into pipeline 40 through which it is fed back into the electrolyser 9. In fact, the medium is rather a foamy substance than a gas, that is why it is appropriate to revert to feedback. The throttle 40 inserted in pipeline 40 produces a pressure drop of 100 Hgmm and the purpose of throttling is to make the liquid flow into the active charcoal filter 22 under suitable pressure.

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The liquid gets through pipe 5 into the cathode space 34 of the electrochemical corrector 32. Electrochemical corrector 32 is supplied by the supply unit 53 with a current of 150 milliampers at 3.5 volts. It physiological salt solution flows through the anode space 35 at a rate 2.5 ml/min. The physiological salt solution gets from the liquid container 37 through control valve 36 into the anode space 35 and from here into the sewage system of the building concerned. The liquid container 37 and the control valve 36 are standard infusion fittings generally used in medical practice.

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Otherwise, instead of the physiological salt solution the UF filtrate leaving the electrolyser 9 (in a way to be described further below) can also be used. Here, bypassing liquid container 37, the UF filtrate can be led from pipeline 42 through pipeline 54 (shown by a dotted line) into anod space 35, and through pipeline 55 into the liquid container 43.

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From the electrochemical corrector 32 the liquid adjusted to 7.4 pH value gets through pipeline 6 first into active charcoal filter 22 and from here into the zeolite filter 23. Because of filtering no organic material fragment will be present in the liquid entering pipeline seven, the organic material residue will be 40 % of that present in the fed-in liquid, the hypochlorite-ion content will be max. 3 mg/l and instead of a part of the K⁺ ions it will contain Na⁺ ions.

The regenerated liquid gets, through pipeline 7, through pump 38 and through pipeline 8 into the outlet-pipe connection 2. and through the latter into the artificial kidney machine. The rated delivery output of the second pump 38 is 600 ml/min, the overpressure produced by it is 760 Hgmm ($\approx 10^5$ Pa).

The difference between the delivery outputs of pump 20 and second pump 38 will have the result that less water will return to the outlet-pipe connection 2 than the quantity entering the equipment through inlet-pipe connection 1. The difference leaves the cycle as UF filtrate through an overflow orifice 56 provided on the electrolyser cell 10 and flows through pipeline 42 into the liquid container 43.

Through the overflow orifice 56 also the gases recirculated from the degassing assembly 28 escape. A part of the gases developing during the electrolysis escape here, so the load imposed on the degassing assembly 18 is by that reduced in advance. These gases escape from liquid container 40 through pipeline 44 and active charcoal filter 45 into the ambient atmosphere.

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Based on the knowledge of how the equipment operates also the required regulation performed by control unit 46 can fully be understood based on a few additional data.

After some corrections of the signals issued by the organic material signal transmitter 47 and hypochlorite signal transmitter 48 made according to the signal of temperature signal transmitter 52, the supply unit 15 is regulated by the control unit 46 in the following way.

As long as the organic material content is above 600 mg/l, the current feeding the electrolytic process with max. 10 amps logarithmically decreases to 5 amps within the range between 600 ml/min. and 200 ml/min, disconnecting below 200 ml/min.

Regulation of the hypochlorite-ion content is simpler, no response of control unit 46 takes place below 100 mg/l hypochlorite ion content, and above this level it stops the electrolytic process.

Signal of the pH signal transmitter is corrected by the control unit 46 according to the signal of the temperatures signal transmitter 49, and the current issued by the supply unit 53 of electrochemical corrector 32 is regulated to the set value of 7.4 pH continuously from either positive or negative deviation.

Based on the signal issued by the pressure signal transmitter 51, the rpm of the motor driving second pump 38 is reduced or increased by means of pulse control mentioned already.

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Finally, the signal of the temperature signal transmitter 52 is directly utilized by the control unit 46 by regulating the supply unit 31 of the cooler 30 in the function of temperature.

Beyond regenerating the dialysis liquid, the equipment can fully perform the disinfection of medically prime importance. For this purpose the inlet-pipe connection 1 and outlet-pipe connection 2 have to be connected with each other, and the entire system has to be filled with physiological salt solution from liquid reservoir 57. From the physiological salt solution hypochlorite ions are formed in the course of the electrolysis, which perform the sterilization. After circulating the solution through a definite period, the liquid may be drained off.

Inlet-pipe connection 1 and outlet-pipe connection 2 may be connected with each other also for within the equipment the purpose of doing sterilization. Of course, for that purpose a manual shut-off fitting has to be inserted into the connecting pipe.

Separate signal transmitters for the indication of organic material content and hypochlorite-ion content are shown in Figure 1, for the sake of simplicity and of showing possible variants. For replacing them, a combined signal transmitter, a measuring device for measuring the organic material and hypocrite ion content, complying with the invention had to be developed.

Vessel 60 shown in Figure 4 is divided in two liquid compartments 61 and 62.

Compartment 61 is fitted with a separate additional bottom 71 having a small boring 63 at its middl.

A pin electrode 65 and a polarizing electrode 66 are placed into the liquid compartment 61. The pin electrode 61 is a platinum filament of 0.5 mm dia. with its point 71 arranged in the vicinity of boring 63. The polarizing electrode 66 is a plate bent to form the shape of letter "C", its material being a platinum coating applied to a titanium base.

Into the liquid compartment 63 a reference electrode made up of silver-silver chloride is immersed.

Liquid compartments 61 and 63 are connected by a solid-electrolyte bridge placed under part 72 to the bottom of vessel 70.

On the side of liquid compartment 61, beside the bottom part 72, a liquid inlet 68, while at the height of the upper edge of polarizing electrode 66, a liquid outlet is provided. The combined signal transmitter can be coupled through these connections into the liquid system of the equipment (e.g., into pipeline 5 of the equipment shown in Figure 1).

The liquid compartment 63 is filled with a 0.9 % solution of sodium chloride.

The polarizing electrode 66 and the reference electrode 67 are connected to a continuously variable potential supply unit 70, whereas the pin electrode 65 is linked with a measuring unit 73. Measuring unit 73 is connected through a control unit 74 with said continuously variable potential supply unit 70. (In the equipment presented in Figure 1 all these are part of the control unit 46, so they are not separately shown.)

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The combined measuring method can be understood from the diagram of Figure 5, in which on the horizontal axis the potentials (E), and on the vertical axis the currents (I) are plotted.

For measuring the organic material content the pin electrode 65 is gradually polarized to anode potential by means of polarizing electrode 66, and the variation of current in the function of time is measured.

As already mentioned further above, the measuring method is based on the fact that the capability of absorbing oxygen is reduced, if organic substances are present in the liquid.

Therefore, the measurement has to be carried out in the range of oxygen adsorption. In spite of increasing anode potential, the current increases but scarcely over a section of the curve. The change starts at 1.18 volts, this is the beginning of the range of oxygen adsorption, from where on the curve starts to rise steeply. It is appropriate to measure the variation in function of time at 10 milliamps, since above this value gas formation sets in, affecting the measurement.

If no organic materials are present in the liquid, the curve setting out from the kneepoint voltage of 1.18 volt reaches the 10-milliamp level in 1.7 s (see curve "a"). Presence of an organic material causes a reduction of oxygen adsorption capability, so a longer time is required to obtain the same adsorption (see curve "b"). The relation can be described as follows:

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where

t: is the time of oxygen adsorption by reaching 10 milliamps a and b: coefficients obtained by experience,

C.: per volume concentration of organic material content

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To demonstrate the order of magnitude of values obtained from the above relation, we remark that a time duration of t = 2.7 s belongs to the value of $C_m = 3$ g/l, which is a very high value in dialysis practice.

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To measure the hypochlorite content the pin electrode 65 is gradually repolarized to cathode potential by means of polarizing electrode 66.

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The already described feature of measuring the hypochlorite content is that in the range of restoring the hypochlorite-ion content a negative peak appears in the current curve. With no hypochlorite ions present in the liquid, the curve, according to the characteristics of hydrogen absorption, hardly raises until about -500 millivolts is reached, than it starts to rise steeply (see curve "c").

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If hypochlorite ions are present in the fluid, said negative current peak appears in the curve before -500 millivolts, and the higher is the hypochlorite ion content, also this peak becomes higher and its range widens (see curves "a1", "d2", "d3"). E.g., with some hypochlorite-ion content said range lies between -500 millivolts and 400 millivolts and the current is -5 milliamps. Thus, the hypochorite-ion content can be measured based on the following equation:

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 $Q^- = c + d \cdot C_{ClO}$

Where

Q: is the negative current value,

c and d: are coefficients determined by experience,

C_{cto}: is the hypochlorite-ion concentration.

The measurements have shown that the accuracy of the above relation depends also on the flow velocity of the liquid and on the washing-off of the pin electrode 65 continuously with the streaming liquid. That is why the liquid is fed into the vessel 60 from the side where the point 71 of the pin electrode 65 is held, to make the liquid enter through the inlet connection 68 flow along the pin electrode 65 and to leave through liquid outlet 69. Experience has shown that the accuracy of measurement is directly proportional with the flow velocity of the liquid, reaching maximum accuracy at 20 cm/s. Within measurements performed by us, the maximum error at this velocity has been 2.8 %, with 2.1 % scattering of results.

The cathode potential is increased further until a negative value of current determined empirically is reached. This value has been fixed as 1.2-times the maximum negative current. This has been found necessary, to allow the performance of measurements automatically, as detailed below:

Pin electrode 65 is polarized to anode potential by means of the continuously variable potential supply unit 70 until +10 milliamps are indicated by the measuring unit 73.

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During this period, the organic material content C_m is determined by measuring unit 73.

When +10 milliamps have been indicated by the measuring unit 73, based on its signal, a command is issued by control unit 74 to the continuously variable potential supply unit 70 to repolarize the pin electrode 65 to anode potential again, and the measuring cycle is repeated from the beginning.

From the above description it will become clear that the negative current value of the measuring process has to be chosen higher than that pertaining to the expected hypochlorite-ion content to prevent the control unit 74 from initiating, even if accidentally, the change of polarity at that peak value.

INDUSTRIAL APPLICABILITY

Since the regeneration of the dialysis liquid of the artificial kidney machine is an extraordinary complex task, considering the number of organic materials being well over a thousand, it will be easy to see, without further examples, that based on the invention, it will be possible to implement a suitable equipment for clearing liquids loaded with any other kinds of organic substances.

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CLAIMS

- 1. Equipment for regeneration of liquids contaminated by organic substances, advantageously dialysis liquids, comprising an electrolyser (9) and an active charcoal filter (22), characterized in that the electrode system (14) of the electrolyser (9) has sheets of which every other is connected to constitute the anodes (11) and cathodes (12), respectively, each cathode (12) at the side of the discharge pipe (17) is extended upwards by a narrow stripe, the liquid-outlet connection being arranged at the level of said stripes (13) perpendicularly to them, whereas the admission pipe (16) of the liquid to the electrode system (14) is accommodated at a point situated the farthest away from the liquid-outlet connection (17) of the electrolyser (9); looking from the inlet-pipe connection (2), the electrolyser (9) comes first and the active charcoal filter comes later, a degassing assembly (18) being inserted between them, further, after said active charcoal filter (2) a zeolite filter (23) is also accommodated.
- 2. Equipment as claimed in Claim 1, characterised in that the degassing assembly (18) consists of a throttle, a pump (20) and a reservoir (21), all connected in series when looking in the direction of liquid flow, said reservoir (21) having a large cross-sectional area as compared to that of the adjoining pipeline (4).
- 3. Equipment as claimed in Claims 1 or 2, characterised in that a second pump (38) is inserted between the zeolite filter (23) and outlet-pipe connection (2).
- 4. Equipment as claimed in any of Claims 1 to 3, characterised in that a cooler (30) is inserted anywhere between the electrolyser (9) and the outlet-pipe connection (2) or second pump (38), if there is one.

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- 5. Equipment as claimed in any of Claims 1 to 4 characterised in that the cooler (30) is integrally built with the reservoir (21) of the degassing assembly (18).
- 6. Equipment as claimed in any of Claims 1 to 5, characterised in that the reservoir (21) of the degassing assembly is of a closed design, said reservoir (21) being provided with a gas discharge line (39) above normal liquid level, connected through a pipeline (40) into said electrolyser (39) on the side of the admission pipe connection also above normal liquid level, with a trottle (41) inserted in the pipeline (40).
- 7. Equipment as claimed in any of Claims 1 to 6, characterised in that between the electrolyser (9) and degassing assembly (18), or between the degassing assembly (18) and outlet pipe connection (2) or second pump (38), if there is one installed, an overflow orifice (56) is inserted, and the delivery output of said second pump (38), if installed, is lower than that of the pump (20) of the degassing assembly (18).
 - 8. Equipment as claimed in any of Claims 1 to 7, characterised in that the overflow orifice (56) is provided on the side of the discharge pipe connection (17) of the electrolyser (9), above normal liquid level, and is connected to an enclosed liquid container (43), the highest point of which is led through an active charcoal filter (45) into the ambient atmosphere.
 - 9. Equipment as claimed in any of Claims 1 to 9, characterised in that an electrochemical corrector (32) is inserted between the degassing assembly (18) and the active charcoal filter (22).

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10. Equipment as claimed in any f Claims 1 to 9, characterised in that an active charcoal filter (22) or a zeolite filter (23) is designed so that the filter housing is a plastic bag (24), in which the filling (26) is confined between two plastic nets, with the connecting pipes (28) inserted between the shut-off ends of the plastic bag (24) and the plastic nets.

11. Equipment as claimed in any of Claims 1 to 10, characterised in that anywhere between the inlet-pipe connection (1) and active charcoal filter (22) an organic material signal transmitter (47), and anywhere between the electrolyser (9) and active charcoal filter (22) a hypochlorite signal transmitter is inserted, further, at least one temperature signal transmitter (49, 52), a pH signal transmitter (56) and a pressure signal transmitter is connected to the inputs of an electronic control unit (46), whereas the outputs are in controlling connection with the supply unit (15) of the electrolyser (9), with the pump (20) of the degassing assembly (18, with the cooler (32), with the second pump (38), if there is one installed, and with the supply unit (53) of the electrochemical corrector (32).

12. Measuring device for measuring organic material and hypochlorite-ion contents consisting of a vessel (60), a pin electrode (65), a polarizing electrode (68) and a reference electrode (67), with the liquid inlet and liquid outlet provided on said vessel (60), characterized in that the polarizing electrode (66) is connected to a continuously variable potential supply unit (70) and the liquid inlet (68) and/or the liquid outlet (69) is located near the point (71) of the electrode (65).

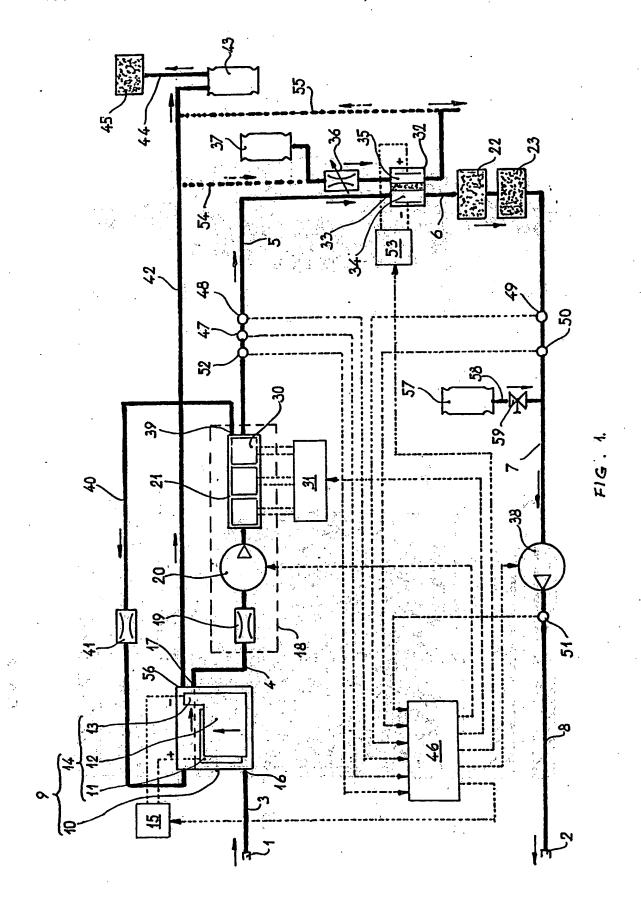
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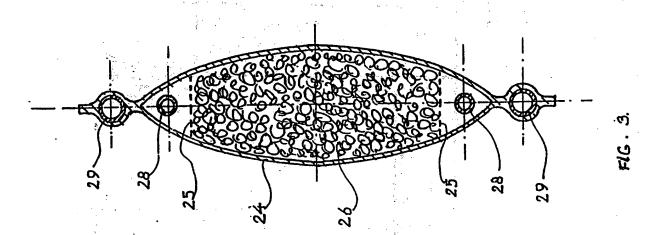
13. Measuring device as claimed in Claim 12, characterised in that the liquid compartments (61, 62) surrounding the reference electrode (67) and pin electrode, separated from each other, are connected through a solid-electrode bridge (64), and the point (71) of the pin electrode is located in the vicinity of the solid-electrical bridge (64).

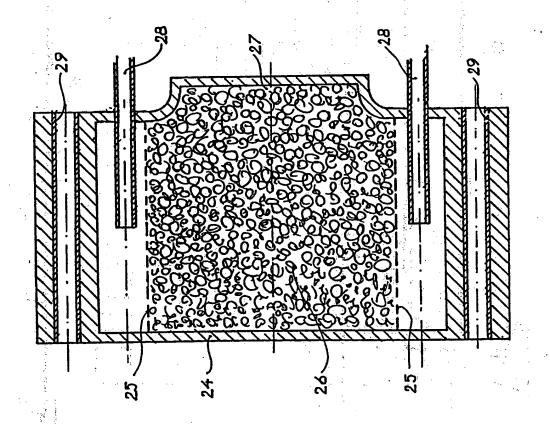
14. Method for measuring the organic material and hypochlorite ion contents in which liquid containing the organic material and hypochorite ions is led into an electrochemical vessel (60) incorporating a pin electrode (65), a polarizing electrode (66), and a reference electrode (67), characterised in that the pin electrode is cyclically polarized in the range of the anode to cathode potential by means of the polarizing electrode (65), and producing on the pin electrode (66), first, a steadily increasing anode potential up to the value of the adsorption potential of oxygen and measuring the time logarithmically proportional with the organic material content, elapsing until a predetermined value of current is reached, then steadily repolarizing the pin electrode (65) from anode potential to cathode potential, and measuring, in the potential range of restoration of hypochlorite content, the level of current directly proportional to the hypochlorite content, maintaining a steady flow of the liquid to be tested in the vicinity of the point of the pin electrode during the measurement.

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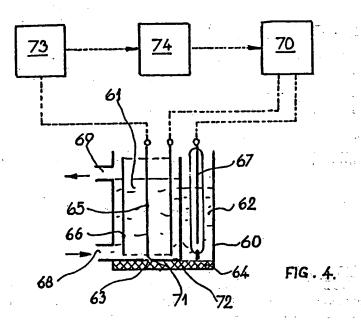
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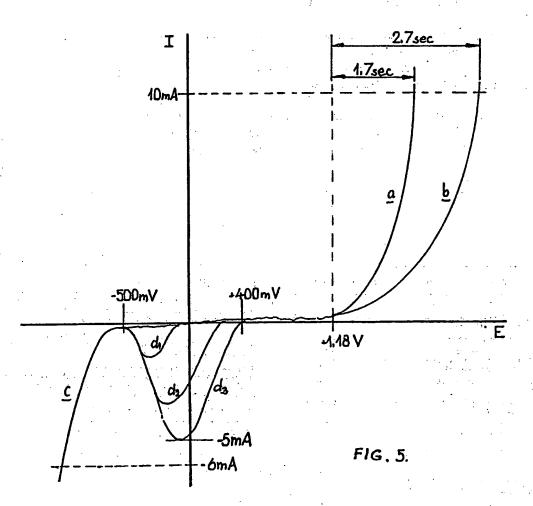






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INTERNATIONAL SEARCH REPORT

International application No.
PCT/HU 94/00026

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A. CLASSIFICATION OF SUBJECT MATTER						
IPC ⁶ : C 02 F 9/00, 1/461, 1/28						
According to International Patent Classification (IPC) or to both national classification and IPC						
	OS SEARCHED umentation searched (classification system followed by c	lessification symbols)			
	IPC ⁶ : C 02 F 9/00, 1/461, 1/28					
Documentatio	n searched other than minimum documentation to the ex	tent that such docume	nts are included in th	e fields searched		
	a base consulted during the International search (name of	data base and, where	practicable, scarca t	erms useu)		
C. DOCUM	MENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where ap	propriate, of the rele	want passages	Relevant to claim No.		
A	A US, A, 5 174 879 (GADKE-FUHRMANN) 29 December 1992 (29.12.92), claims 1,12; fig.					
A	Patent Abstracts of Japan, unsection C, vol. 7, no. 161, 1 The Patent Office Japanese Gono. 58-70 881 (NIHON GIJUTSU)	1				
P,A	P,A Patent Abstracts of Japan, unexamined applications, section C, vol. 18, no. 248, 12 May 1994 (12.05.94), The Patent Office Japanese Government, page 140 C 1198, no. 6-31 278.					
			.			
Further	documents are listed in the continuation of Box C.	X See pater	nt family annex.			
"A" documento be of p	categories of cited documents: It defining the general state of the art which is not considered particular relevance ocument but published on or after the international filling date	date and not in the principle of "X" document of	n conflict with the appl or theory underlying the particular relevance; the	e claimed invention cannot be		
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Date of the a	ctual completion of the international search	Date of mailing of	the international se	arch report		
,	cember 1994 (07.12.94)		r 1994 (28.			
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INTERNATIONAL SEARCH REPORT Information on patent family members

International application No. PCT/HU 94/00026

Im Recherchenbericht	Datum der	Mitglied(er) der	Datum der
angeführtes Patentdokument	Veröffentlichung	Patentfamilie	Veröffentlichung
Patent document cited	Publication	Patent family	Publication
in search report	date	ember(s)	date
Document de brevet cité	Datu de	Mecbre(s) de la	Date de
dans le rapport de recherche	publication	famille de brevets	publication
US A 5174879	29-12-92	CA AA 2037758 DE A1 4007151 EP A1 445792	08-09-91 19-09-91 11-09-91

